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Evidence for Liquid-Liquid Phase Transitions in the Transition Metals

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In this paper we report the first experimental evidence for the existence of a liquid-liquid phase transition(LLPT) in the transition metals. The transition is evident from discontinuities in the melting slope measured at high pressure. The discovery of LLPTs constitutes the strongest evidence for the presence of polymorphic structures in transition metal liquids at high pressure, and confirms the thesis that they are responsible for the relatively low melting temperatures, low melting slopes, and unusual phase diagrams.

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In earlier reports[1,2] we proposed that, in order to explain the apparent discrepancy between the diamond anvil and shock wave melting measurements of Mo and Ta, a liquid-liquid phase transition(LLPT), or liquid-glass transition, had to be present in the phase diagram. LLPTs are characterized by liquids of the same composition, but with different densities, and different atomic configurations, often referred to as polymorphs. In this paper we present the first experimental evidence for LLPTs in transition metals. It is now well established that elements with partially filled p -electron valence shells have directional bonding and exhibit an LLPT. Some examples are carbon[3,4], silicon[5,6], nitrogen[7,8] and phosphorous[9,10]. Bellisent et al.[11] interpreted the structure of liquid As, obtained from neutron diffraction experiments, as the consequence of a strong Peierles distortion in the half-filled $3p$ -band[12].

The partially filled d -electron bands of transition metals also have the potential for a Peierles distortion, and directional bonding. The low melting slopes of transition metals has been attributed to directional d -electron bonding leading to the formation of

preferred local structures with five-fold icosahedral or polytetrahedral short range order(ISRO) resulting from Peierls/Jahn-Teller(P/JT) distortions[12,13]. Evidence for the presence of ISROs in transition metal liquids is now well documented and are referenced in our earlier reports[1,2]. ISROs introduce geometric frustration inhibiting solidification, and their presence as soluble impurities increases the communal entropy, further favoring the liquid stability and lowering the freezing temperature. Since ISROs are denser than the pure atomic liquid, pressure enhances the concentration of local structures. Therefore, it should come as no surprise, that pure non-alloyed transition metal liquids, with partially filled *d*-bands, exhibit polymorphic behavior, and a pressure-induced LLPT.

The scarcity of experimental evidence for LLPTs in transition metals is at least partially due to the relatively high temperatures characteristic of these liquids. With the advent of the laser-heated diamond-anvil-cell technique it has now become possible to access melting curves of transition metals up to nearly 200 GPa and 4000K. The experimental method employed on a wide variety of solids, including on the transition metals, has been described and referenced in earlier reports[14-17]. Melting is detected in a laser-heated diamond-anvil cell by warming a sample and observing the onset of speckle motion in the melt. Measurements are checked for reproducibility at least six times for every pressure point in each sample. We wish to emphasize that the laser speckle technique is very well suited to distinguish between solid-solid, and solid-liquid transitions. When a solid-liquid transition is crossed, by increasing the laser power, speckle motion is maintained even when the laser power is held constant. On the other hand, when a solid-solid transition is crossed one observes a discontinuous, single event change in the laser speckle pattern.

Plotted in figures 1-4 are the melting measurements for a representative set of transition metals, Cu, Ni, Ti, Y, Mo and Ta. With the exception of Cu, all the transition metals studied, including those not included here, Fe, Co, Cr, V and W, exhibited an abrupt discontinuity in the melting slopes indicative of an LLPT. The sharpness suggests that the LLPTs may be first order-like, but masked by the uncertainty in the temperature. The experimental data for all these metals had been reported earlier[11-

13]. However the presence of LLPTs was initially overlooked because of a reliance on data smoothing fitting functions.

Cu has a filled $3d$ -band, and a linear Lindemann-like melting curve and lacks any evidence of an LLPT that might result from P/JT distortions in the liquid. As such, Cu provides a useful reference system, or benchmark, for comparison with the other metals. Since, with few exceptions, transition metals do not undergo solid-solid phase changes along the melting curve, a sudden decrease in the melting slope implies an increase in the liquid density and an increase of the communal entropy, which may be attributed to an LLPT.

Figure 1 shows a plot of the Cu[17] and Ni[1,17-19] melting measurements, figure 2 shows Cu and Ti, and figure 3 has Y[20]. These data plots illustrate that Ni, Ti and Y exhibit abrupt discontinuities in their melting curves which is indicative of an LLPT. In the case of Ni and Cu both have the same melting slopes up to 18 GPa. At this pressure, the Ni melting slope shows a sharp decrease. In the case of Ti and Cu, at low pressure, they have very different melting slopes. This shows that at low pressure Ni has a relatively smaller concentration of ISROs and consequently behaves like Cu. In contrast, Ti starts out with a significantly lower melting slope than Cu showing that it has a relatively larger concentration of ISROs than Ni. Yttrium, which has a single d -electron has the narrowest d -band, and the sharpest discontinuity in its melting slope. This pattern of behavior is to be predictable, since the Jahn-Teller distortion favors the narrow bands of the early transition metals. Since $dT/dP \sim 0$ for Ti and Y at pressures above the transition, then $\Delta V \sim 0$ and the new liquid phase is necessarily solid-like or glassy.

Some understanding of the ISROs in a liquid may be drawn from the work of Lee et. al.[21], who reported x-ray diffraction measurements of electrostatically levitated droplets of Ni and Ti. From an analysis of the liquid structure factors they determined that the short-range order of liquid Ni is non-distorted icosahedral, while in Ti the icosahedral order is significantly distorted. Lee and Lee[22], employing first principles density functional calculations of Ni and Ti clusters, found a significant distortion of the Ti cluster icosahedron resulting in short bonds, but no meaningful distortion of the Ni

icosahedron. Lee and Lee also found that the distortion in Ti becomes more severe when additional atoms are added to the Ti cluster creating larger clusters. The combined results of Lee et al.[21,22] are in agreement with the diffraction measurements and are consistent with the fact that the P/JT effect is stronger for the early metals [1].

In the case of Cs, which has $5d$ -electron character, and in a broad sense may be considered as a very early transition metal, Falconi et al.[23,24] have interpreted structural changes and density increases from x-ray diffraction patterns above 3.9 GPa that mark the change from a simple to a locally complex liquid. Their analysis “strongly suggests the existence of dsp^3 electronic hybridization”, a P/JT distortion.

The melting curve measurements of Mo and Ta are shown in figure 4. Both metals exhibit discontinuities in the melting slopes near 30-40 GPa implying the presence of LLPTs. The original measurements for Mo have been confirmed by Santamaria et al.[25] using x-ray diffraction techniques to detect melting, and for Ta by Errandonea et al.[26], also using x-ray diffraction and by Foata-Prestavoine et al. employing the speckle motion detection method[27]. Nevertheless, the DAC melting measurements, particularly the low melting slopes, have been controversial because of apparent disagreements with shock melting experiments of Mo[28,29] and Ta[30]. In fact, the dynamic shock and static DAC measurements do not conflict, since they cover different regions of the phase diagram. In combination they provide new insights into the phase diagrams of transition metals [1,2]. We limit further discussion here to Mo, because the shock data for this metal is more complete, and in any case the properties of the Mo and Ta differ little.

Plotted for Mo, in figure 5, are the DAC melting measurements, the Hugoniot (dashed curve), and two data points, at 200 GPa and 400 GPa, where discontinuities in the longitudinal sound speed have been detected in shock experiments. Hugoniot temperatures were calculated[29]. The shock discontinuity near 200GPa(~ 4000 K) has been interpreted as a bcc-hcp transition, and the discontinuity at 400 GPa($\sim 10,000$ K) as melting from a solid to a liquid. Figure 5 includes a proposed LLPT involving an abrupt structural change between the phases; as referred to previously[2] as liquid and Phase II, and connecting the discontinuity in the Mo melting at 30 GPa to the 400

GPa(10,000K) shock transition. Near 400 GPa, the liquid is an *ideal* homogeneous fluid and Phase II is a phase in which long-range order is absent but pressure induces a high degree of local ordering.

Although, evidence is lacking to support the argument that the 200 GPa transition is bcc-hcp[2,31], Mo does in fact retain some shear strength along the Hugoniot in the regime between 200 GPa and 400 GPa. In this case, liquid 2 would have had to undergo a continuous pressure-induced change starting from the liquid near 30 GPa to a glass-like Phase II at 200 GPa. A linear extrapolation of the DAC melting curve to 200 GPa predicts a melting temperature near 3330 K, below the 4000 K calculated for the shock transition. This suggests that the shock sound speed discontinuity at 200 GPa is from the bcc solid to a glassy state, and that at the 400 GPa transition the Hugoniot crosses the LLPT from a glass-like Phase II to a liquid. While very little theoretical effort has been directed to pressure-induced glass transformations, the parallel of a liquid to glass transformation studied by cooling can be instructive. For example, Doye et al.[32], employing a potential that favored the formation of five-fold coordinated liquid structures found that cooling lead to the formation of a polymeric network of linked icosahedrons.

An alternative interpretation of the Mo phase diagram, based mainly on computer simulations of the solid-liquid melting[33,34], discounts entirely the validity of the DAC measurements, and argues that a bcc-liquid melting curve connects directly from melting at 1 bar to the 400 GPa shock discontinuity. However, these simulations treat the liquid as purely atomic (i.e hard-sphere or inert gas-like) and neglect the influence that locally preferred structures have on melting and a phase diagram with LLPTs.

The important new result in this report is the discovery of an LLPT in transition metal liquids. With exception of Cu, the transition is ubiquitous having been detected in all of the ten transition metals so far studied. The presence of LLPTs provide the strongest evidence for the presence of polymorphic structures in transition metal liquids, and confirms the physical origin of the low melting temperatures, and low melting slopes measured in the diamond-anvil cell.

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Figure captions

Fig. 1. Cu and Ni melting measurements. Cu(open circles)[17], Ni(filled circles)[1,17]. Ni(filled squares)[18]. Ni(filled triangles)[19].

Fig. 2. Cu and Ti melting measurements. Cu (open circles)[17], Ti(filled circles)[15].

Fig. 3. Y melting measurements.(filled circles)[20].

Fig. 4. Mo and Ta melting measurements, (empty circles)[14].

Fig.5. Mo phase diagram. DAC measurements(filled circles)[15], with extrapolation to 200 GPa(long dashed curve). Hugoniot with calculated temperatures (short dashed curve)[29]. Pressures at which discontinuities in the longitudinal sound speeds were detected on the Hugoniot (filled squares with error bars)[28,29].

Figure 1

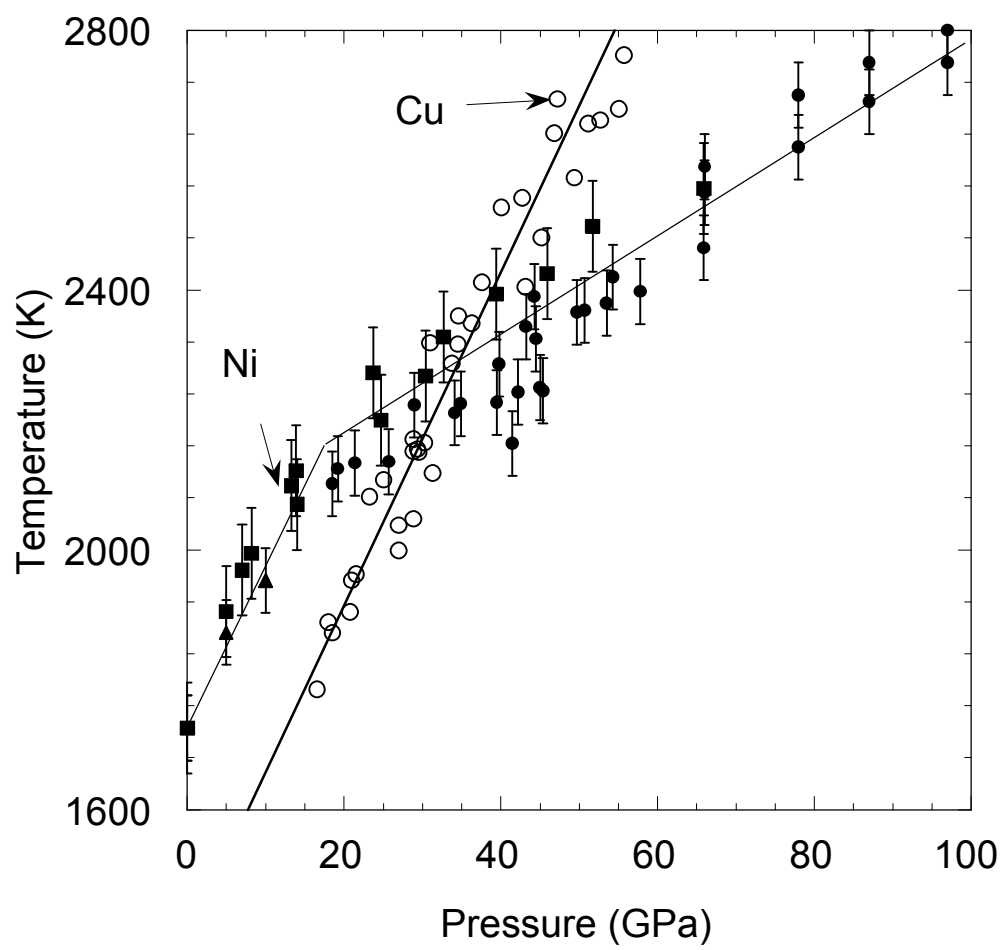


Figure 2

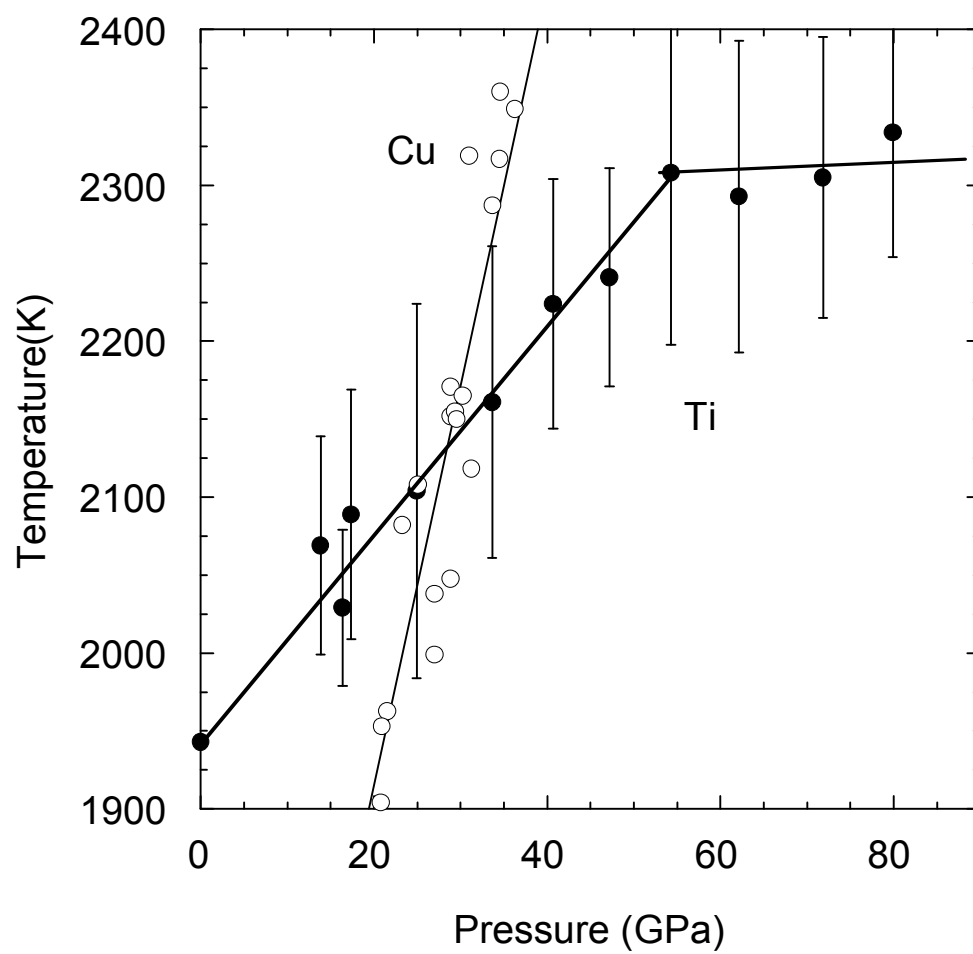


Figure 3

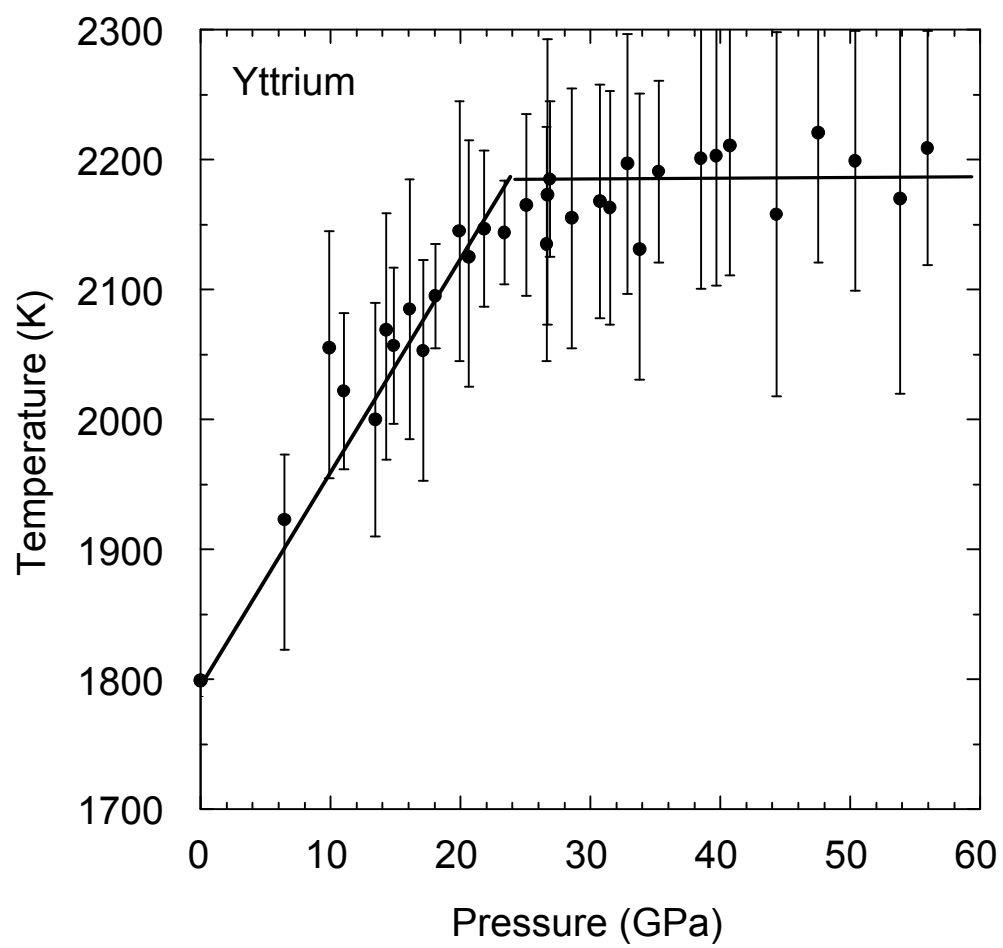


Figure 4

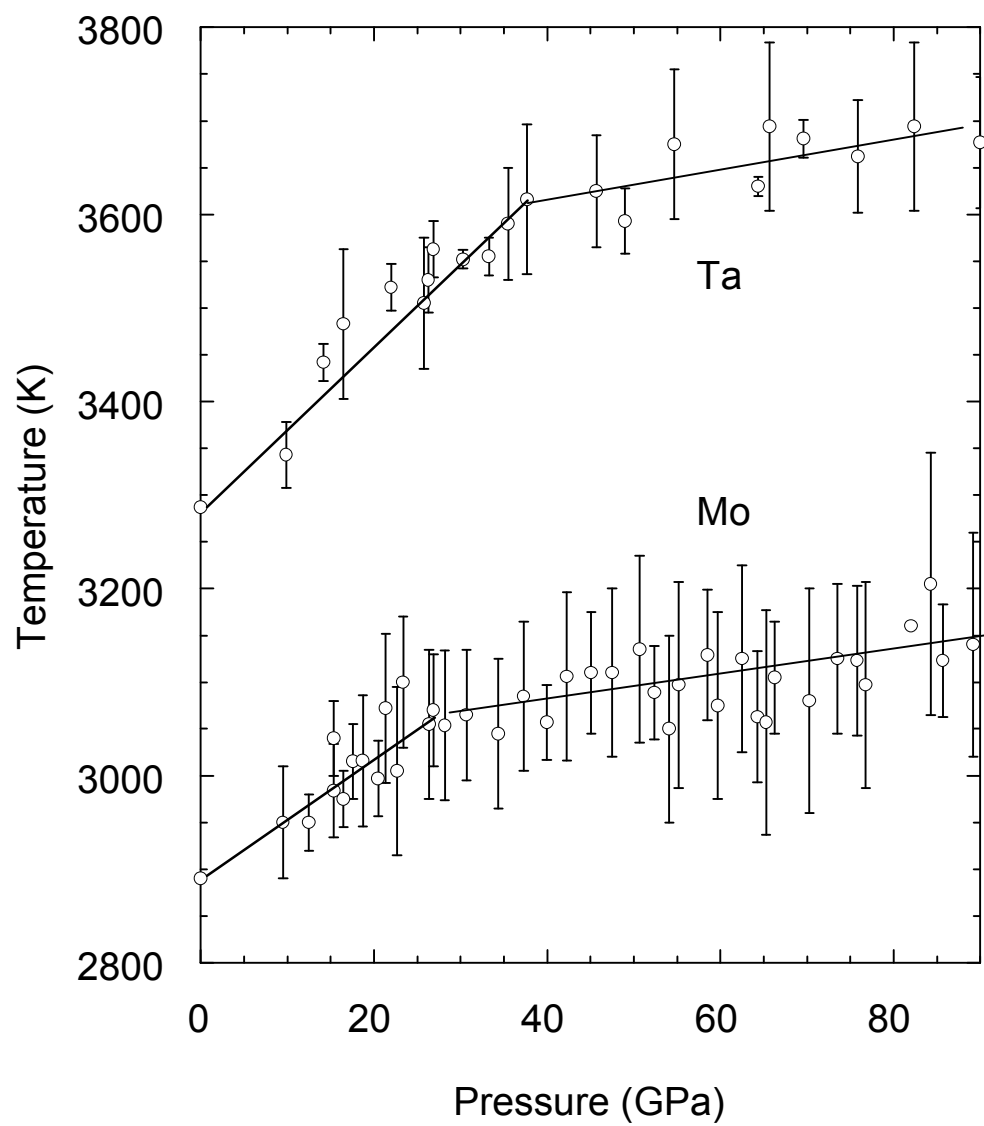


Figure 5

